Ferroelectricity in Perovskite Superlattices by Atomic-Level Simulation

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Ceramic Epitaxial Films

SCIENTIFIC ACHIEVEMENT

We have recently developed and validated an atomic-level approach to the simulation of the phase behavior of perovskite materials including $KNbO_3$ and $BaTiO_3$, both of which manifest three different ferroelectric phases, and $KTaO_3$ and $SrTiO_3$, both high-dielectric-constant paraelectrics. Using atomic-level simulation methods, we have determined the ferroelectric and dielectric properties of coherent $KNbO_3/KTaO_3$ superlattices from zero temperature to above the Curie transition. The in-plane behavior at zero temperature is essentially bulk-like with an abrupt jump in the polarization at the interfaces; the Curie temperature in the plane appears to be only weakly modulation-length dependent. By contrast, the polarization in the modulation direction at zero temperature is continuous through the interfaces with the interior of the $KTaO_3$ layers remaining polarized for modulation lengths of up to $\Lambda = 160$ unit cells. An investigation of the switching behavior shows that for $\Lambda > 24$ unit cells, each $KNbO_3$ layer behaves essentially independently. For $\Lambda < 12$, the $KNbO_3$ layers interact so strongly with each other that the superlattice essentially behaves as a single artificial ferroelectric structure. Consistent with experiments on this system, the Curie temperature for the transition from a polarized to unpolarized state in the modulation direction decreases approximately linearly with modulation length, Λ, for $\Lambda > 12$; for smaller modulation lengths, it is essentially Λ-independent.

SIGNIFICANCE

There is a long history of using atomic-level simulation to explore the microstructure-property relationship in metals, semiconductors and ceramics. Our simulations show that the properties of ferroelectric/paraelectric composites are determined by the interplay between the strong electric fields associated with the intrinsic electric dipoles of the ferroelectric with the induced polarization in the paraelectric. The materials specific atomic-level potentials for the $KNbO_3/KTaO_3$ system, and our recently developed potentials for the $BaTiO_3/SrTiO_3$ system, open up to simulation a large number of problems on the interplay of ferroelectricity and microstructure.

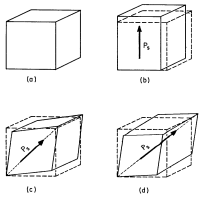
PHASES OF $KNbO_3$

cubic
T > 708K

tetragonal
T = 488K - 701K

orthorhombic
T = 210K - 488K

rhombohedral
T < 210K



ATOMISTIC SIMULATION OF PEROVSKITES

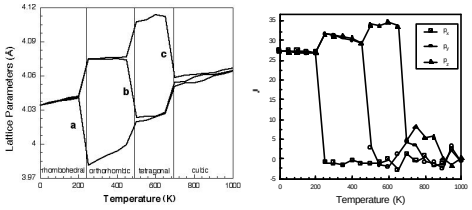
Payoff

- **Atomic-level information**
- **1 - 1000 Å (N ~ 10^6)**
- **Simulate microstructure**
- **Non-zero temperature**
- **Materials science of ferroelectricity**

Challenge

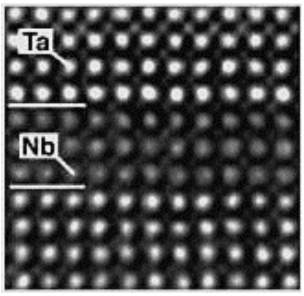
- **Capture small energy difference in different structures at the atomic level**

REPRODUCES PHASE DIAGRAM CORRECTLY



Sepliarsky et al., APL 76, 2986 (2000)

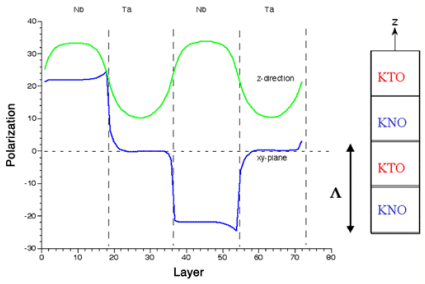
FERROELECTRIC / PARAELECTRIC ($KNbO_3$ / $KTaO_3$) SUPERLATTICES



H. M. Christen et al., APL, 72, 2535 (1998)

- **Epitaxial $KTaO_3/KNbO_3$ superlattices**
- **Grown in [001] orientation on $KTaO_3$**
- **Small lattice mismatch between $KTaO_3$ and $KNbO_3$ leads to coherent interfaces**

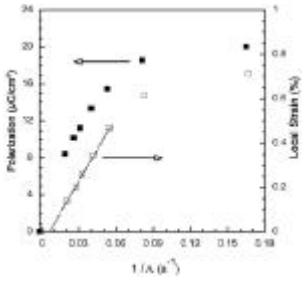
POLARIZATION IN SUPERLATTICE



- **Polarization in x-y plane is bulk-like**
- **Polarization in modulation direction (z-direction) is strongly coupled**

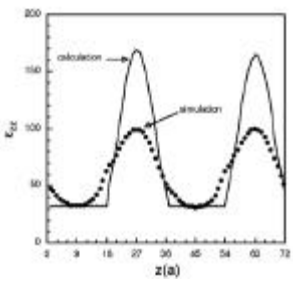
Sepliarsky et al, Phys. Rev. B 64, 0601010(R), (2001); J. Appl. Phys. 90, 4509-4519 (2001).

STRONG COUPLING ACROSS $KNbO_3/KTaO_3$ INTERFACES



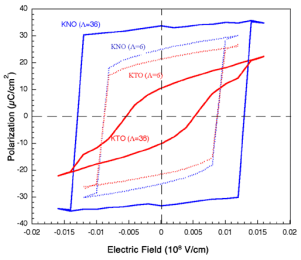
- **Polarization at center of $KTaO_3$ layers zero for $\Lambda > 160$**

DIELECTRIC PROPERTIES



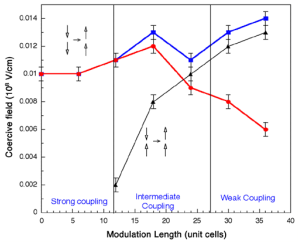
- **Dielectric constant in $KTaO_3$ determined by strain and high electric field**

SWITCHING BEHAVIOR



- **Small Λ - $KNbO_3$ and $KTaO_3$ layers form single artificial ferroelectric structure**
- **Large Λ - Weak coupling between layers**

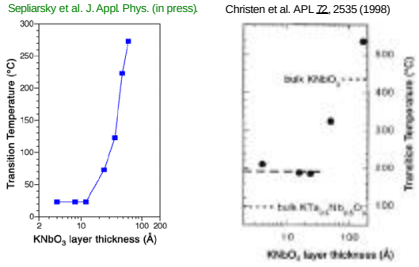
LONG-RANGED FERROELECTRIC INTERACTIONS



FINITE-TEMPERATURE PROPERTIES

Simulation
Sepliarsky et al. J. Appl. Phys. (in press).

Experiment
Christen et al. APL 72, 2535 (1998)



- **T_c in modulation direction strongly Λ dependent**

CONCLUSIONS

- **Atomic-level simulation can describe ferroelectric behavior of $KNbO_3$ and $BaTiO_3$**
- **Long-ranged ferroelectric interaction in ferroelectric/paraelectric superlattices**
- **Phase behavior**
  - **in-plane:**
    - **Curie temperature independent of Λ**
  - **in modulation direction:**
    - **Curie temperature strongly dependent on Λ**

OTHER STUDIES

$BaTiO_3$/ $SrTiO_3$

Ferroelectric properties of solid solutions

Polarization rotation during switching of perfect crystal

FUTURE WORK

Ferroelectric domains and domain dynamics

Grain boundaries, thin films and surfaces

$LiNbO_3$

Mesoscale simulation of ferroelectrics

FWP 58305